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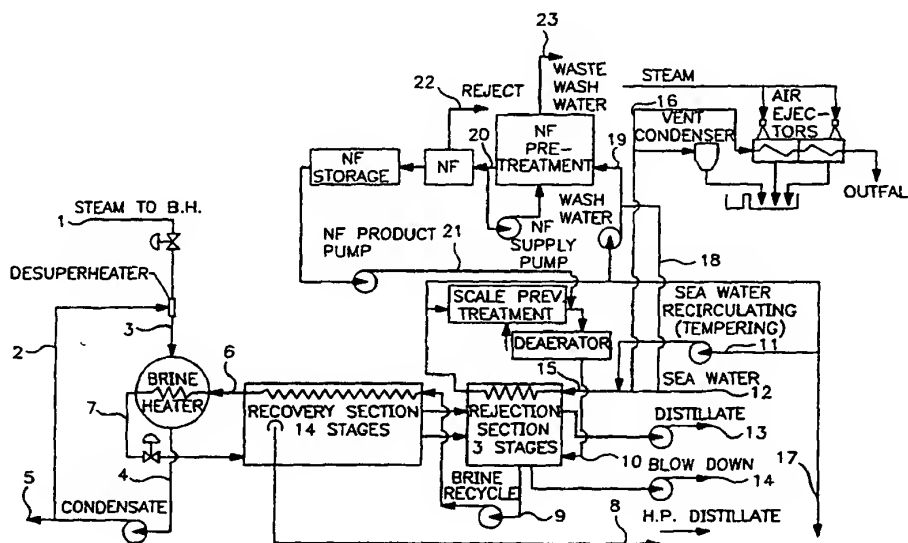
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(54) Title: A SALT WATER DESALINATION PROCESS USING ION SELECTIVE MEMBRANES



(57) Abstract: The invention is directed to an improved desalination process to produce potable water. The process represents an improvement of hybrid of membrane and desalination technologies. The improvement of the invention comprises the operation of an ion selective membrane at a variable pressure as a function of the cost of electricity to form a softened salt water that is blended in variable proportions, to increase the top operating temperature of the desalination system and increase recovery of potable water, with untreated salt water.

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## A SALT WATER DESALINATION PROCESS USING ION SELECTIVE MEMBRANES

This application claims priority to U.S. provisional patent application having the  
5 application number 60/150,159, filed August 20, 1999.

### Background of the Invention

#### 1. Technical Field

The present invention relates to a water purification process and more particularly, it relates to an improved process for the desalination of salt water by the strategic use of ion  
10 selective membranes to form a variable make-up that is fed to a desalination unit to produce a water product of potable quality.

#### 2. Description of Related Art

The basic processes for the desalination of salt water to produce a water product of potable quality include, for example, multistage flash distillation, multieffect distillation, reverse  
15 osmosis and vapor compression distillation. Each of these processes are well established technologies having their own unique characteristics and limitations. The high content of scale forming ions, saline and other impurities found in untreated salt water has a negative impact on the efficiency, energy consumption and maintenance of large scale plants which employ any of these conventional desalination processes. Due to such high concentrations of impurities, it is  
20 commonly known to add antiscaling chemicals to the feed or equipment to minimize the adverse consequences of scale forming ions.

Multistage flash distillers which are in common use worldwide for large scale desalination projects are limited in their performance by the maximum brine temperature (top brine temperature or TBT) that can be used in the process. At temperatures higher than the maximum,  
25 scale inhibitors are ineffective and significant fouling of the internal surfaces will rapidly occur. This can be expensive and time consuming to remove.

Membrane technology has been used in the pre-treatment of salt water to reduce the high ionic content of salt water relative to fresh water. For example, U.S. Patent No. 4,723,603 discloses a process for removing precursor ions from an injection water which formed insoluble  
30 salt precipitates in situ when they contacted resident ions already present in a subterranean hydrocarbon-bearing formation. The precursor ions of the insoluble salt precipitates are removed by means of a RO membrane.

More importantly for desalination, WO 99/16714 discloses the combination of membrane technology with the basic desalination processes to form a drinkable water product. According to this document, saline water containing a high content of hardness scaling ions is passed through a nanofiltration membrane to form make-up to a desalination system. Nanofiltration softening  
5 membranes are used for the selective removal of hardness scale forming ions and other impurities to soften seawater. Due to nanofiltration treatment, the make-up has a reduced ionic content when it passes through the desalination system. It is reported that there is a reduction of scaling and fouling tendency when this combination of nanofiltration and desalination systems is employed. However, the document does not suggest any means of taking advantage of the inter-  
10 relationship among certain conditions, e.g., pressure, temperature and make-up, to achieve an optimal system and recovery.

It will be seen that in spite of these disclosures, there is still a great need for a process that optimizes the combination of these two technologies to improve the operating conditions, efficiency and yield of this type of hybrid desalination systems.

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### Summary of the Invention

Accordingly, the present invention is directed to an improved process for desalinating salt  
4 water at optimal operating conditions. In accordance with the invention, the content of hardness ions is sufficiently reduced from the make-up to a desalination system such that the desired top  
20 operating temperature, or desired recovery of potable water product, of any desalination system can be achieved. As a direct result, a number of advantages are realized which include a more cost-efficient operation of desalination plants, a reduction in the energy consumption of such plants and an increased yield of potable water. In addition, the use of chemical anti-scaling agents is advantageously minimized or completely eliminated. These and other advantages are achieved  
25 by specific improvements of hybrid desalination systems based on combined membrane and conventional desalination technologies.

As used throughout the following discussion, the term "salt water" shall mean to include water having a significant concentration of hardness or scale forming ions, e.g., sulfate, calcium, magnesium and bicarbonate ions. Sources of salt water which are contemplated by the present  
30 invention include, without limitation, ocean water, gulf water, reject, blowdown and recycle brine in solution and impaired water containing soluble salts having an ionic content of hardness ions in excess of 1,500 mg/liter.

In accordance with the present invention, a first stream of salt water containing a high concentration of hardness ions is passed through an ion selective membrane to form a softened

salt water product having a reduced content of hardness ions. The softened salt water is blended with a second stream of salt water containing a high concentration of hardness ions to form a feed to a desalination system. The feed is then introduced to the desalination system to form a water product of potable quality. The softened salt water content of the feed is at least 5%. The  
5 desalination system may be one or more desalination processes including reverse osmosis, multistage flash distillation, multieffect distillation and vapor compression distillation.

In one embodiment of the invention, a nanofiltration (NF) membrane is employed as the ion selective membrane. A NF membrane softening system comprising one or more of such NF membranes is combined with a multistage flash (MSF) distillation plant. The NF system is  
10 introduced after the MSF-deaerator. In one embodiment, untreated saltwater is first subjected to a deaeration pre-treatment step before entering the NF system. Alternatively, a stream of softened sea water exits the NF system and then enters the MSF-deaerator for the removal of non-condensable gases from the softened water. A portion of the stream of untreated salt water is pre-heated by the heat of a reject stream exiting the reject section of the desalination plant before  
15 passing through the NF membrane system. The MSF distillation system is operated at a TBT of 95-180°C. The NF membrane system is operated at a variable pressure of 5-60 bar. To be discussed in more detail, the ability to vary the operating pressure of the NF system provides a means of control over the ionic content and quantity of softened salt water.

In another embodiment of the invention, the softened salt water is stored in a buffer  
20 system from where it is blended with a stream of untreated salt water to form the feed to the desalination system. Alternatively, the softened salt water that is stored in the buffer system is injected into the desalination system. Additionally, this reserved supply of softened salt water is used to form a cluster feeding system wherein the softened salt water is fed from the buffer system to two or more desalination systems for blending with untreated salt water.

25 In yet another embodiment, a partial stream of reject brine, blowdown or recycled brine produced during the desalination process is subject to a nanofiltration step and recycled through the desalination system.

### Brief Description of the Drawings

30 Fig. 1 is a schematic flow diagram of an integrated hybrid desalination process using a hybrid of nanofiltration and desalination systems in accordance with the invention.

Fig. 2 is a schematic flow diagram illustrating the process of the invention as applied to multistage flash distillation in accordance with the invention.

Fig. 3 is a schematic flow diagram showing the integration of a nanofiltration plant with an existing multistage flash distiller utilizing the process of the invention.

Fig. 4 is a graph showing the percentage increase in distillate production from a hybrid of nanofiltration and multistage flash distillation systems.

5 Fig. 5 is a graph showing the reduction in salinity by nanofiltration as a function of applied pressure.

Figs. 6-9 plot the anhydrite scaling index against NF treated make-up blend ratios and at various concentration factors.

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### Description of the Preferred Embodiments

The prior art desalination processes which are based on combined ion selective membrane and conventional water desalination systems are significantly improved with the present invention. Having read and understood the features and principles of the invention as presently described and shown in the figures, an experienced engineer in designing, manufacturing and operating water  
15 desalination systems of the type contemplated by this invention would be able to practice the invention and realize its benefits.

According to one aspect of the invention, the improvement resides with the discovery that  
4 the make-up to the desalination plant can be purposefully configured at any stage of operation to achieve higher top operating temperatures and increased yields of potable water. Surprisingly, it  
20 has been discovered that even a partial elimination of calcium and sulfate ions from the feed will advantageously improve the performance of desalination plants. This improvement is not suggested by the prior art. Specifically, by using a feed comprising variable proportions of softened and untreated salt water, the concentration of hardness ions is sufficiently reduced, thereby allowing a beneficial increase in the TBT of the desalination process. Higher operating  
25 temperatures provide an increase in productivity, recovery and performance at lower energy and chemical consumption. As a result, the cost of desalinated water production, including operation and maintenance, when compared to the prior art hybrid systems is dramatically reduced.

In accordance with the present invention, one or more ion selective membranes is introduced into a desalination system for the purpose of providing flexibility in managing the ionic  
30 content of the make-up to the desalination plant. Any of the known and art-recognized desalination systems can be used in the present invention. Desalination processes such as reverse osmosis, multistage flash distillation, multi-effect distillation and vapor compression distillation are known throughout the relevant industry and sufficiently described in the literature. The operation

of any of these conventional systems is considered to be well within the purview of the skilled artisan.

Similarly, ion selective membranes are known in the art. As contemplated by the present invention, the membrane is preferably one which selectively prevents the hardening ions from passing across it while at the same time allowing the water and harmless ions to pass across it. For the express purposes of the invention, the membrane is used for the selective removal of hardness ions to soften salt water. The selectivity of a membrane is a function of the particular properties of the membrane, including the pore size or electrical charge of the membrane. Accordingly, any of the known and commercially available ion selective membranes which meet these criteria can be used with the invention. For example, a polyamide membrane is particularly effective for selectively preventing sulfate, calcium, magnesium and bicarbonate ions from passing across it. A polyamide membrane having the trade name SR90-400 (Film Tec Corporation) or Hydranautics CTC-1 is preferred. A membrane element comparison of Filmtec SR90 400 and Hydranautics CTC-1 is shown in Table 1:

TABLE 1  
MEMBRANE ELEMENTS COMPARISON

	FILMTEC SR90 400	HYDRANAUTICS CTC-1
Maximum applied pressure	600 psig (4.16 Mpa)	600 psig (4.16 Mpa)
Maximum operating temp.	45° C	45° C
Maximum flow rate	72 gpm (16.4 m <sup>3</sup> /h)	75 gpm (17 m <sup>3</sup> /h)
Maximum feed SDI	5	5
Membrane area	3.72 x 10 <sup>5</sup> cm <sup>2</sup> (400 ft <sup>2</sup> )	3.72 x 10 <sup>5</sup> cm <sup>2</sup> (400 ft <sup>2</sup> )
Element length/diameter	101.6cm x 20.32cm (40" x 8")	101.6cm x 20.32cm (40" x 8")

The following sequence of Tables 2-5 demonstrates that the use of ion selective membranes will remove a large proportion of the most significant scaling compounds from sea water make-up to be fed to a desalination unit. The typical chemical composition of MSF recycle and the average sea water feed of Arabian Gulf sea water is shown in Table 2 below. However pursuant to the invention, a first stream of salt water having a high concentration of hardness ions is passed through an ion selective membrane to form a softened salt water. The softened sea water is then blended with normal untreated sea water to lower the scaling potential of the make-up. The data of Table 3 is representative of the performance of a NF membrane. In addition, Table 3 shows the removal of sulfate, magnesium, calcium and bicarbonate ions in much larger percentages than monovalent ions of sodium, potassium and chloride. Typical reductions of sulfate, calcium, magnesium and bicarbonate ions are shown in Table 4 when a NF membrane Filmtec SR90 is used. Table 4 demonstrates the ability to employ NF technology to achieve a

higher system rejection of scaling ions in the first stage versus subsequent stages of nanofiltration. Finally, Figure 5 shows performance of nanofiltration membranes as developed by Hydranautics.

TABLE 2  
CHEMICAL COMPOSITION OF MSF RECYCLE AND AVERAGE SEAWATER FEED

Recycle Typical Gulf MSF		Sea water Quality at Doha	
Ionic Strength	1.4078		
	ppm	Concentration	mg/l
Sodium	21,013	12,300	± 20
Calcium	786	570	± 45
Magnesium	2,627	1,700	± 150
Bicarbonate	209	185	± 18
Chloride	37,190	24,000	± 700
Sulfate	5,229	3,400	± 300
Carbonate	21	14	± 8
TDS	67,075	47,000	± 2000

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TABLE 3  
NANOFILTRATION NF MEMBRANE PERFORMANCE

ION	SEAWATER (ppm)	NF PERMEATE (ppm)	SYSTEM % REJECTION
Sodium	11,200	10,050	10
Potassium	370	320	14
Calcium	400	309	23
Magnesium	1,400	330	76
Chloride	19,750	19,000	4
Sulfate	2,650	48	98
Bicarbonate	140	20	86
Total	35,910	30,715	

TABLE 4  
NF MEMBRANE SOFTENING

	Sea water Feed	First Stage	Second Stage
Sulfate	2700	22	90
Calcium	410	108	204
Magnesium	1310	440	690
Bicarbonate	150	29	72

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TABLE 5  
NF MEMBRANE PERFORMANCE

ION	SEAWATER (ppm)	NF PERMEATE (ppm)	SYSTEM % REJECTION
Sodium	12,100	10,442	13.7
Magnesium	1,100	713	35.2
Chloride	18,100	16,073	11.2
Sulfate	2,580	21	99.2

However, the advantages and improvements of the present invention do not reside with the mere combination, as disclosed by WO 99/16714, of an ion selective membrane and a desalination process for the production of potable water. Rather, the previously unrecognized advantage of the present invention resides, in part, with the introduction of a feed of variable proportions of softened and untreated salt water to a desalination system to increase the top operating temperature of the system and increase the yield of potable water. In contrast, WO 99/16714 teaches a hybrid process wherein 100% of the feed is subjected to a nanofiltration pre-treatment process prior to being feed to a desalination unit. Furthermore, the ion selective membrane can be advantageously operated, in accordance with the invention, at a variable pressure as a function of energy costs to achieve a significant improvement in the cost-efficiency of the desalination plant. There is no illustration or suggestion in WO 99/16714 that a variable percentage of make-up and/or operating pressure would advantageously improve the performance of desalination plants.

In accordance with the broad aspects of the invention, a first stream of salt water containing a high concentration of hardness ions is passed through an ion selective membrane to form a softened salt water having a reduced concentration of hardness ions. The softened salt water is blended with a second stream of untreated salt water containing a high concentration of hardness ions to form a feed to a desalination system. The feed is then introduced to a desalination system to form a water product of potable quality. The percentage of softened salt water is at least 5% of the make-up. It should be recognized that the source of softened salt water can also be supplied by any salt water stream that has already passed through the ion-selective membrane and/or desalination system and that is recycled through the desalination system. It is the reduced concentration of hardness ions that is determinative of the suitability of softened salt water for blending to form make-up to a desalination system as contemplated by the present invention.

A further protection against scale forming ions, in particular carbonate and magnesium hydroxide scale, is the addition of stoichiometric amounts of acid, e.g., 10-100 ppm of sea water feed, prior to passing the sea water through an ion selective membrane. Examples of acid that are suitable for this purpose include hydrochloric and sulfuric acid. The addition of acid protects the ion selective membrane, improves rejection and filtration, and reduces alkalinity. Furthermore, the combination of the acid and membrane treatment affords an additional protection to the desalination plant by reducing or optionally eliminating the use of antiscalants.



Figure 1 illustrates a basic flow diagram of an integrated hybrid desalination process using a hybrid of selective ionic membrane and desalination systems including multistage flash distillation, multieffect distillation, vapor compression distillation and reverse osmosis desalination. As shown in Figure 1, a stream of intake salt water is blended with a portion of make-up stream from the heat reject section of the distillation plant. The make-up stream from the heat reject section is characterized by a reduced content of hardness ions. The sea water stream to be subjected to NF treatment undergoes pre-treatment to remove suspended solids by means of fixed media filtration or micro- or ultra-filtration equipment. The sea water stream with a silt density index (SDI) of 5 or better is pressurized between 5-80 bars below the osmotic pressure of the solution and enters the NF membrane unit. The NF membrane assembly is composed of several arrays with a typical two to one ratio. Each of the NF modules contains from 4-8 NF elements. The treated, softened sea water stream is then blended with untreated salt water to form make-up to any of the shown distillation units.

Another important and advantageous aspect of the invention is the recognition that the ion selective membrane can be operated at a variable pressure as a function of the cost of electricity to maximize the energy efficiency and yield of the desalination plant. Generally speaking, the ion selective membrane is operated at pressures of 5-80 bars, but in all cases, below the osmotic pressure of the salt water stream to be treated. At the upper range of operating pressures, there is an increased reduction of scaling ions and total salinity. However, operation of the ion selective membrane system at such higher pressures requires a greater demand for energy utilization. Therefore, the variability of operating pressures as a function of the cost of electricity optimizes the energy efficiency and yield of the desalination plant.

This option is particularly advantageous in regions like the Middle East where there are wide seasonal and daily variations with regard to the utilization of power. For example, in summer when there is a maximum peak demand for energy at an associated higher cost, the ion selective membrane system is operated at the lowest possible pressure, thereby minimizing energy consumption without adversely effecting a reduction of scaling ion content. Conversely, at off-peak power demand during the winter, the ion selective membrane system is operated at the upper range of operating pressures to increase the productivity and efficiency of the desalination plant. The ability to control the operating pressure of such systems is within the skill of the experienced plant operator. This advantage enables the plant operator to determine the ionic content and quality of the softened water product at the most energy efficient conditions at the time of operation.

The invention also provides an option to recycle a portion of a brine stream through the ion selective membrane system. The treated stream is then combined with the recycle flow with a sufficient reduction in scaling ions to permit an increase in the top operating temperatures of the desalination system. Similarly, in another embodiment, an ion selective membrane system is introduced at the point of brine blowdown where the concentration of scaling ions is the highest. A portion of the blowdown is then subjected to a nanofiltration step and recycled to the desalination system.

An advantageous embodiment of the present invention is the combination of a NF membrane system with MSF distillation. The principles of MSF distillation are simple. Sea water feed is pressurized and heated to the maximum plant temperature. When the heated liquid is discharged into a chamber maintained slightly below the saturation vapor pressure of the liquid, a fraction of its water content flashes into steam. The flash steam is then stripped of suspended brine droplets as it passes through a mist eliminator and condenses on the exterior surface of heat transfer tubing. The condensed liquid drips into trays as hot product water.

The unflashed brine enters a second chamber, or stage, where it flashes to steam at a lower temperature, thereby producing an additional quantity of product water. Simultaneously, the distillate from the first stage passes to the distillate tray in the second stage and gives up some of its heat. The flash-cooling process is repeated from stage to stage until both the cooled brine and the cooled distillate are finally discharged from the plant as blowdown brine and product water, respectively.

The recirculating stream flowing through the interior of the tubes that condenses the vapor in each stage serves to remove the latent heat of condensation. In so doing, the circulating brine is pre-heated to almost the maximum operating temperature of the process, simultaneously recovering the energy of the condensing vapor. This portion of the multistage flash distillation plant is called the "heat recovery" section. The pre-heated brine is finally brought up to the maximum operating temperature in a brine heater supplied with steam from an external source. At the cool end of the plant, a separate set of tubes is installed in several of the stages in a "heat rejection" section to remove the waste heat. A small fraction of this coolant becomes pre-heated make-up water.

According to one embodiment of the invention, a NF membrane softening system is introduced in a MSF distillation system after the MSF-deaeration unit. As a result of this arrangement, oxygen, residual chlorine and reduce corrosion are removed from the stream of untreated salt water before it enters the NF membrane system. Specifically, the stream of salt water to be subjected to NF treatment is subjected to a deaeration pre-treatment step before

passing through the NF membrane system. Alternatively, a stream of softened salt water exiting the NF system is blended with a stream of untreated salt water. The blend passes through the MSF-deaeration unit before entering the distillation unit. A portion of the stream of untreated salt water is pre-heated by the heat of a reject stream of the desalination system before passing through the NF membrane system. In contrast to conventional MSF desalination plants operating at temperatures between 95-112°C, the MSF distillation system of the invention is operated at a temperature of 95-180°C. This top temperature is beyond that which is currently achievable by existing methods and specifically by the use of chemical additives.

Figure 2 provides a schematic representation of the process of the invention as applied to MSF. A projected commercial operation utilizing NF and MSF is represented in Figure 3. The reference numbers appearing in Figure 3 refer to the operating conditions, as set forth in Tables 8-11, at the identified stages of the system. As shown in Figure 3, the NF unit is introduced as a system on the warm feed that is part of the sea water cooling system before entering the MSF-deaerator. The recovery of water heat and the warming of the stream of sea water entering the nanofiltration system significantly increases the fluxes and productivity of the NF elements. By this arrangement, it is possible to remove oxygen, residual chlorine and carbon dioxide from the feed stream and reduce its corrosiveness before the stream enters the MSF unit. The carbon dioxide released in the NF system can be recovered for beneficial uses, e.g., the post-treatment of the recovered water product.

Figure 4 shows that the NF system and process permits a safe increase in TBT, e.g., up to 125°C. This same Figure demonstrates a percentage increase in distillate production from MSF plants using NF systems of the present invention. As shown in Figure 5, a reduction of total salinity by the NF system of the invention as a function of applied pressure permits not only a reduction of scaling compounds but also a partial reduction in total salinity. The reduction of total salinity as achieved by the invention has the benefit of reducing boiling point elevation, improving the thermodynamic properties of brine, improving heat transfer coefficient and optimizing the make-up requirements. The use of the present invention will also reduce fouling factors as shown in Table 6:

TABLE 6  
FOULING FACTORS WITH NF IN COMPARISON  
WITH CONVENTIONAL MSF PERFORMANCE

Fouling factor @ temp °C. in m <sup>2</sup> K/W	125°C	120°C	110°C	90°C and lower <
Brine heater w/ NF	0.000210	0.000200	0.000180	0.000180
Brine heater w/o NF	NA	NA	0.00258	0.000260
Recovery Section w/NF	NA	NA	0.000120	0.000105
Recovery Section w/o NF	NA	NA	0.000150	0.000150

In accordance with another embodiment of the invention, softened salt water is stored in a buffer system. This stored supply of softened water is available for blending with untreated salt water to form make-up that is introduced to the desalination system. In the absence of blending, the softened salt water that is stored in the buffer system can be injected directly into the desalination system. The supply of reserved softened salt water can be used to form a cluster feeding system wherein the softened salt water is fed to two or more desalination systems for blending with untreated salt water. The implicit advantage of this arrangement is the ability to determine the ionic content of the feed that is eventually passed to the desalination system. Consequently, it is possible to adjust operating conditions of the plant to control energy consumption. Moreover, the buffer system permits the shutdown of the ion selective membrane system without effecting the continuous operation of the desalination unit.

A simulation was conducted to evaluate the technical and economic feasibility of NF pre-treatment of make-up water to a typical MSF distiller in accordance with the process of the invention. The reference plant is an existing 5mgid MSF distiller in the Middle East. The reference plant was chosen as being relatively new (less than four years old) and comprises two identical 5mgid units. The plant is situated in the Arabian Gulf and operates as part of a power and desalination plant. The plant operates with a TBT between 106°C and 112°C. The guaranteed unit heat rate at 106°C TBT and 38°C sea water (summer conditions) is 7.5 kg of distillate per 2326 kJ of heat input.

The NF design of the study was based on coagulation and multimedia filtration for pre-treatment with Dow Filtec membranes, operating at manufacturer recommended conditions with a system recovery rate of 75%. Blending calculations were performed using varying proportions of NF product water with heated sea water to produce a modified blended MSF make-up water. The results are shown in Table 7 below. The resulting blended MSF make-up water was then used as the input water for purposes of the simulation.

TABLE 7

CALCULATION OF BLENDED MSF MAKE-UP WATER QUALITY  
(VARYING PROPORTIONS OF NF MEMBRANE PRODUCT & SEAWATER)

% NF 1 product)	100	90	80	70	60	50	40	30	20	10	0
% sea water	0	10	20	30	40	50	60	70	80	90	100
	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm	ppm
Na	13935	14026	14117	14208	14299	14389	14480	14570	14660	14750	14840
K	336	352.5	369	385.5	401.9	418.3	434.8	451.1	467.4	483.7	500
Mg	687	773.9	860.7	947.4	1033.9	1120.3	1206.5	1292.6	1378.5	1464.3	1550
Ca	226	263.7	301.3	338.8	376.3	413.8	451.1	488.4	525.7	562.9	600
Sr	7	8.1	9.2	10.3	11.4	12.5	13.6	14.7	15.8	16.9	18
Ba	0.03	0.034	0.038	0.042	0.046	0.05	0.054	0.058	0.062	0.066	0.07
Cl	24089	24307	24525	24742	24959	25175	25392	25608	25823	26038	26253
SO <sub>4</sub>	106	441.9	777.2	1112	1446	1779.9	2113	2445.6	2777.6	3109.1	3440
CO <sub>3</sub>	0	3.8	7.7	11.5	15.3	19.1	22.9	26.7	30.5	34.2	38
HCO <sub>3</sub>	80	84.8	89.7	94.5	99.3	104.1	108.9	113.7	118.5	123.2	128
OH	0	0	0	0	0	0	0	0	0	0	0
TDS*	39466	40262	41057	41850	42642	43432	44223	45011	45797	46582	47367
pH	7.8	7.92	8	8.05	8.09	8.12	8.15	8.16	8.18	8.19	8.2

5 \*TDS = total dissolved solids

The anhydrite scaling index (SI) against NF treated make-up blend ratios was then calculated and plotted at various concentration factors (CF). At each of four possible operating temperatures (115°C, 120°C, 125°C and 130°C), the maximum limit on allowable scaling index  
10 (SI) is shown Figures 6-9. From this data, it is evident that the concentration factor (CF) affects the required NF blend ratio significantly. For example, an increase in CF from 1.4 to 1.5 requires an increase in NF blend ratio of approximately 10%.

Figure 3 shows a process flow diagram illustrating a proposed integration of a NF plant and a MSF plant such as the reference MSF plant used in the simulation. As a result of the  
15 integration pursuant to the process of the invention, it is possible to raise the TBT of the MSF plant, i.e., a typical 5migd multistage flash installation operating at 106°C, to 125°C with 25% nanofiltration and increase output by 33.8%. Similarly, the TBT of the same MSF plant can be raised to 121°C TBT with 10% nanofiltration and an increased output of 25%.

Tables 8-11 are heat and mass balance flow sheets for different alternatives (125°C TBT  
20 and 121°C TBT) operating in accordance with the invention. The flow sheets of Tables 8 and 10 are directed to summer conditions when the temperature of sea water is in the region of 38°C

whereas Tables 9 and 11 are directed to winter conditions when the temperature of sea water is 15°C. Reference number 13 of Figure 3 and the corresponding column 13 of Tables 8-11 relate to distillate production from the NF-MSF system in accordance with the invention.

TABLE 8

125°C TBT; 38°C SW; 20% NF MAKE-UP

Stream	1	2	3	4	5	6	7	8	9	10	11
Flow (Kg/s)	49.504	1.76	51.263	51.263	49.504	3024	3024	7	3024	857	0
Temp (°C)	195	132.42	130	132	132	115.7737	125	120	51.203	49.87	62.84
Pressure (bar g)	13.73	5	3	2.9	4	2.35	2	1.9	6.86		
Salinity (ppm)						6.73	6.73				

TABLE 8 (continued)

125°C TBT; 38°C SW; 20% NF MAKE-UP

Stream	12	13	14	15	16	17	18	19	20	21	22	23*
Flow (Kg/s)	2278	352	505	1801	236	1115	241	241	229	171	58	660
Temp (°C)	38	50.09	51.73	38	38	52.84	38	38	38	38	38	38
Pressure (bar g)	4.25			3.4	4.25	2.8	4.25	4.25	2		1.5	1
Salinity (ppm)	4737			4737	4737	4737	4737	4737	4737	3950	7100	4737
*Typical intermittent flows												

TABLE 9

125°C TBT; 15°C SW; 20% NF MAKE-UP

Stream	1	2	3	4	5	6	7	8	9	10	11
Flow (Kg/s)	56.177	2	58.177	58.177	56.177	3024	3024	7	3024	932	651
Temp (°C)	195	133.56	130	132	132	114.5188	125	120	42.102	41.75	42.68
Pressure (bar g)	13.73	3	3	2.9	4	2.2	2	1.9	6.88		2.8
Salinity (ppm)						6.74	6.74				

TABLE 9 (continued)

125°C TBT; 15°C SW; 20% NF MAKE-UP

Stream	12	13	14	15	16	17	18	19	20	21	22	23*
Flow (Kg/s)	1426	391.19	540	1801	236	182	40	262	250	186	63	660
Temp (°C)	15	39.84	42.26	25	15	42.68	15	38	38	38	38	15
Pressure (bar g)	4.25			3.4	4.25	2.8	4.25	4.25	2		1.5	1
Salinity (ppm)	4737			4737	4737	4737	4737	4737	4737	3950	7100	4737
*Typical intermittent flows												

TABLE 10

121°C TBT; 38°C SW; 10% NF MAKE-UP

Stream	1	2	3	4	5	6	7	8	9	10	11
Flow (Kg/s)	46.359	1.63	47.992	47.992	46.359	3024	3024	7	3024	818	0
Temp (°C)	195	128.03	130	128	128	112.1674	121	115.5	51.508	51.22	52.68
Pressure (bar g)	13.73	5	3	2.5	4	2.2	2	1.9	6.99		
Salinity (ppm)						6.91	6.91				

TABLE 10 (continued)

121°C TBT; 38°C SW; 10% NF MAKE-UP

Stream	12	13	14	15	16	17	18	19	20	21	22	23*
Flow (Kg/s)	2152	331.1	485	1801	236	1065	115	115	109	82	28	330
Temp (°C)	38	49.96	51.62	38	38	52.68	38	38	38	38	38	38
Pressure (bar g)	4.25			3.4	4.25	2.8	4.25	4.25	2			
Salinity (ppm)	4737			4737	4737	4737	4737	4737	4737	3950	7100	4737
*Typical intermittent flows												

TABLE 11

121°C TBT; 16°C SW; 10% NF MAKE-UP

Stream	1	2	3	4	5	6	7	8	9	10	11
Flow (Kg/s)	53.45	1.89	55.337	55.337	53.45	3024	3024	7	3024	900	683
Temp (°C)	195	129.22	130	129	129	110.8144	121	115.5	41.817	41.75	42.17
Pressure (bar g)	13.73	5	3	2.6	4	2.2	2	1.9	6.98		
Salinity (ppm)						6.91	6.91				

TABLE 11 (continued)

121°C TBT; 16°C SW; 10% NF MAKE-UP

Stream	12	13	14	15	16	17	18	19	20	21	22	23*
Flow (Kg/s)	1376	374.6	525	1801	236	202	20	126	120	90	30	330
Temp (°C)	15	39.39	41.84	25	15	42.17	15	38	38	38	38	15
Pressure (bar g)	4.25			3.4	4.25	2.8	4.25	4.25	2			
Salinity (ppm)	4737			4737	4737	4737	4737	4737	4737	3950	7100	4737
*Typical intermittent flows												

The data of Tables 8-11 demonstrate that the TBT and output of a MSF plant are substantially increased through the use of NF pre-treatment and blending of the make-up water.

- 15 These improvements are achieved by blending a stream of softened salt water and untreated salt water to form a feed to the desalination system. As a result, it is possible to operate the MSF plant at a higher TBT. Advantageously, the increased output is attained at lower operating costs for the NF and MSF plants.

Although the invention has been described in terms of preferred embodiments, it is to be understood that the present invention may be changed or modified without departing from the spirit and scope of the invention as claimed.



What is claimed is:

1. An improved desalination process to produce potable water which comprises:
  - (a) passing a first stream of salt water containing a high concentration of hardness ions through an ion selective membrane to form a softened salt water having a reduced content of hardness ions;
  - 5 (b) blending the softened salt water with a second stream of untreated salt water containing a high concentration of hardness ions to form a feed to a desalination system;
  - (c) introducing the feed to the desalination system to form a water product of potable quality, wherein the improvement comprises the introduction of a feed of variable proportions of softened and untreated salt water to the desalination system to increase the top operating temperature of
  - 10 the system and increase recovery of potable water.
2. The desalination process according to claim 1, wherein the softened salt water content of the feed is at least 5%.
- 15 3. The desalination process according to claim 1, wherein the feed is passed through at least one desalination system selected from the group consisting of reverse osmosis, multistage flash distillation, multieffect distillation and vapor compression distillation.
4. The desalination process according to claim 3, wherein the desalination system is thermal
- 20 driven and selected from the group consisting of multistage flash distillation and multieffect distillation.
5. The desalination process according to claim 3, wherein the desalination system is electric driven and selected from the group consisting of reverse osmosis and vapor compression
- 25 distillation.
6. The desalination process according to claim 3, wherein the desalination system is multistage flash distillation.
- 30 7. The desalination process according to claim 6, wherein the multistage flash distillation system is operated at a temperature of 95-180°C.
8. The desalination process according to claim 1 or 6, wherein the ion selective membrane is a nanofiltration membrane.

9. The desalination process according to claim 8, wherein the first stream of salt water is subjected to a deaeration pre-treatment step after passing through a softening system comprised of one or more nanofiltration membranes.
- 5
10. The desalination process according to claim 9, wherein the first stream of salt water is pre-heated by the heat of a reject stream of the desalination system before deaeration.
11. The desalination process according to any one of claims 1 or 4-7, wherein the ion selective  
10 membrane is operated at a variable pressure of 5-80 bar.
12. The desalination process according to claim 11, wherein the ionic content and quantity of softened salt water varies with the operating pressure of the ion selective membrane.
- 15 13. The desalination process according to claim 1, wherein the softened salt water is stored in a buffer system.
14. The desalination process according to claim 13, wherein the softened salt water stored in the  
buffer system is blended with the second stream of untreated salt water to form the feed to the  
20 desalination system.
15. The desalination process according to claim 13, wherein the softened salt water stored in the buffer system is injected into the desalination system.
- 25 16. The desalination process according to claim 1, wherein the softened salt water is fed by a cluster system to two or more desalination systems and blended with the second seawater stream of each system.
17. The desalination process according to claim 1, wherein the desalination system produces  
30 brine containing water selected from the group consisting of reject, blowdown and recycled brine which is partially subjected to a nanofiltration step and recycled through the desalination system.
18. The desalination process according to claim 1, wherein a stoichiometric amount of acid is added to the first stream before that stream passes through the ion selective membrane.

19. An improved desalination process to produce potable water which comprises:
- (a) passing a first stream of salt water containing a high concentration of hardness ions through an ion selective membrane to form a softened salt water product having a reduced content of hardness ions, wherein the ion selective membrane is operated at variable pressure as a function of the cost of electricity;
  - (b) blending the softened salt water with a second stream of untreated salt water containing a high concentration of hardness ions from a buffer system to form a feed to a desalination system;
  - (c) introducing the feed from the buffer system to the desalination system to form a water product of potable quality,
- wherein the improvement comprises the operation of the ion selective membrane at a variable pressure as a function of the cost of electricity to form the softened salt water that is blended in variable proportions, to increase the top operating temperature of the desalination system and increase recovery of potable water, with the untreated salt water.
20. The desalination process according to claim 19, wherein the feed is passed through at least one desalination system selected from the group consisting of reverse osmosis, multistage flash distillation, multieffect distillation and vapor compression distillation.
21. The desalination process according to claim 19, wherein the ion selective membrane comprises a nanofiltration membrane softening system.
22. The desalination process according to claim 21, wherein the ion selective membrane is operated at a variable pressure of 5-80 bar.
23. The desalination process according to claim 19 and 22, wherein the ionic content and quantity of softened salt water varies with the operating pressure of the ion selective membrane.
24. An improved desalination process which comprises:
- (a) blending a first stream of softened salt water having a substantially reduced concentration of hardness ions with a second stream of untreated salt water containing a high concentration of hardness ions to form a feed to a desalination system, and
  - (b) passing the feed through the desalination system to form a water product of potable quality,

wherein the improvement comprises the introduction of a feed of variable proportions of softened and untreated salt water to the desalination system to increase the top operating temperature of the system and increase recovery of potable water.

5 25. The desalination process of claim 24, wherein the stream of softened salt water is obtained by passing untreated salt water across an ion selective membrane to reduce the ionic content of the first stream.

10 26. The desalination process of claim 24, wherein the stream of softened salt water is brine containing water produced by the desalination system, and wherein the brine containing water is selected from the group consisting of reject, blowdown and recycled brine.

## AMENDED CLAIMS

[received by the International Bureau on 19 January 2001 (19.01.01);  
original claims 24 and 26 amended; other claims unchanged (2 pages)]

19. An improved desalination process to produce potable water which comprises:
- (a) passing a first stream of salt water containing a high concentration of hardness ions through an  
5 ion selective membrane to form a softened salt water product having a reduced content of  
hardness ions, wherein the ion selective membrane is operated at variable pressure as a function of  
the cost of electricity;
- (b) blending the softened salt water with a second stream of untreated salt water containing a high  
concentration of hardness ions from a buffer system to form a feed to a desalination system;
- 10 (c) introducing the feed from the buffer system to the desalination system to form a water product  
of potable quality,  
wherein the improvement comprises the operation of the ion selective membrane at a variable  
pressure as a function of the cost of electricity to form the softened salt water that is blended in  
variable proportions, to increase the top operating temperature of the desalination system and  
15 increase recovery of potable water, with the untreated salt water.
20. The desalination process according to claim 19, wherein the feed is passed through at least  
one desalination system selected from the group consisting of reverse osmosis, multistage flash  
distillation, multieffect distillation and vapor compression distillation.
- 20
21. The desalination process according to claim 19, wherein the ion selective membrane  
comprises a nanofiltration membrane softening system.
22. The desalination process according to claim 21, wherein the ion selective membrane is  
25 operated at a variable pressure of 5-80 bar.
23. The desalination process according to claim 19 and 22, wherein the ionic content and  
quantity of softened salt water varies with the operating pressure of the ion selective membrane.
- 30 24. An improved desalination process which comprises:
- (a) blending a first stream of softened water having a substantially reduced concentration of  
hardness ions with a second stream of untreated salt water containing a high concentration of  
hardness ions to form a feed to a desalination system, wherein the source of the first and second  
streams are different, and

- (b) passing the feed through the desalination system to form a water product of potable quality, wherein the improvement comprises the introduction of a feed of variable proportions of softened and untreated salt water to the desalination system to increase the top operating temperature of the system and increase recovery of potable water.

10

25. The desalination process of claim 24, wherein the stream of softened salt water is obtained by passing untreated salt water across an ion selective membrane to reduce the ionic content of the first stream.

26. The desalination process of claim 24, wherein the stream of softened salt water is brine containing water produced by the desalination system, and wherein the brine containing water is selected from the group consisting of reject, blowdown, distillate, and recycled brine.

## STATEMENT UNDER ARTICLE 19

Applicant respectfully submits this communication to amend the claims of the referenced application under Article 19. Two (2) replacement sheets are submitted as part of this communication to replace the corresponding sheets of claims filed with the original application.

Claims 1-23 and 25 are unchanged. Claims 24 and 26 are replaced by amended claims 24 and 26, respectively.

The differences between claims 24 and 26, as originally filed, and amended claims 24 and 26, respectively, are shown as follows (where underlining indicates text to be inserted):

24. An improved desalination process which comprises:

(a) blending a first stream of softened salt water having a substantially reduced concentration of hardness ions with a second stream of untreated salt water containing a high concentration of hardness ions to form a feed to a desalination system, wherein the source of the first and second streams are different, and

(b) passing the feed through the desalination system to form a water product of potable quality, wherein the improvement comprises the introduction of a feed of variable proportions of softened and untreated salt water to the desalination system to increase the top operating temperature of the system and increase recovery of potable water.

26. The desalination process of claim 24, wherein the stream of softened salt water is brine containing water produced by the desalination system, and wherein the brine containing water is selected from the group consisting of reject, blowdown, distillate, and recycled brine.

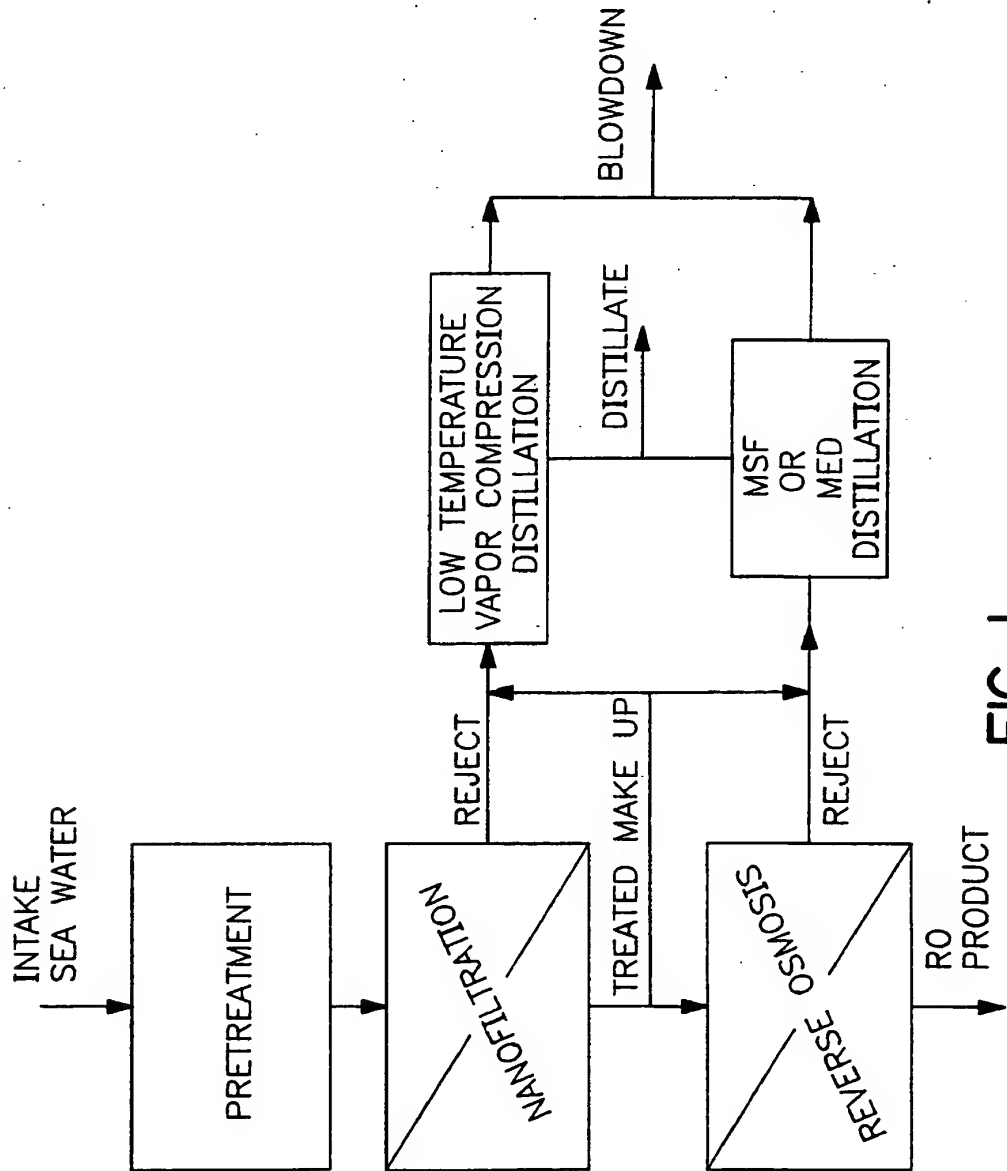
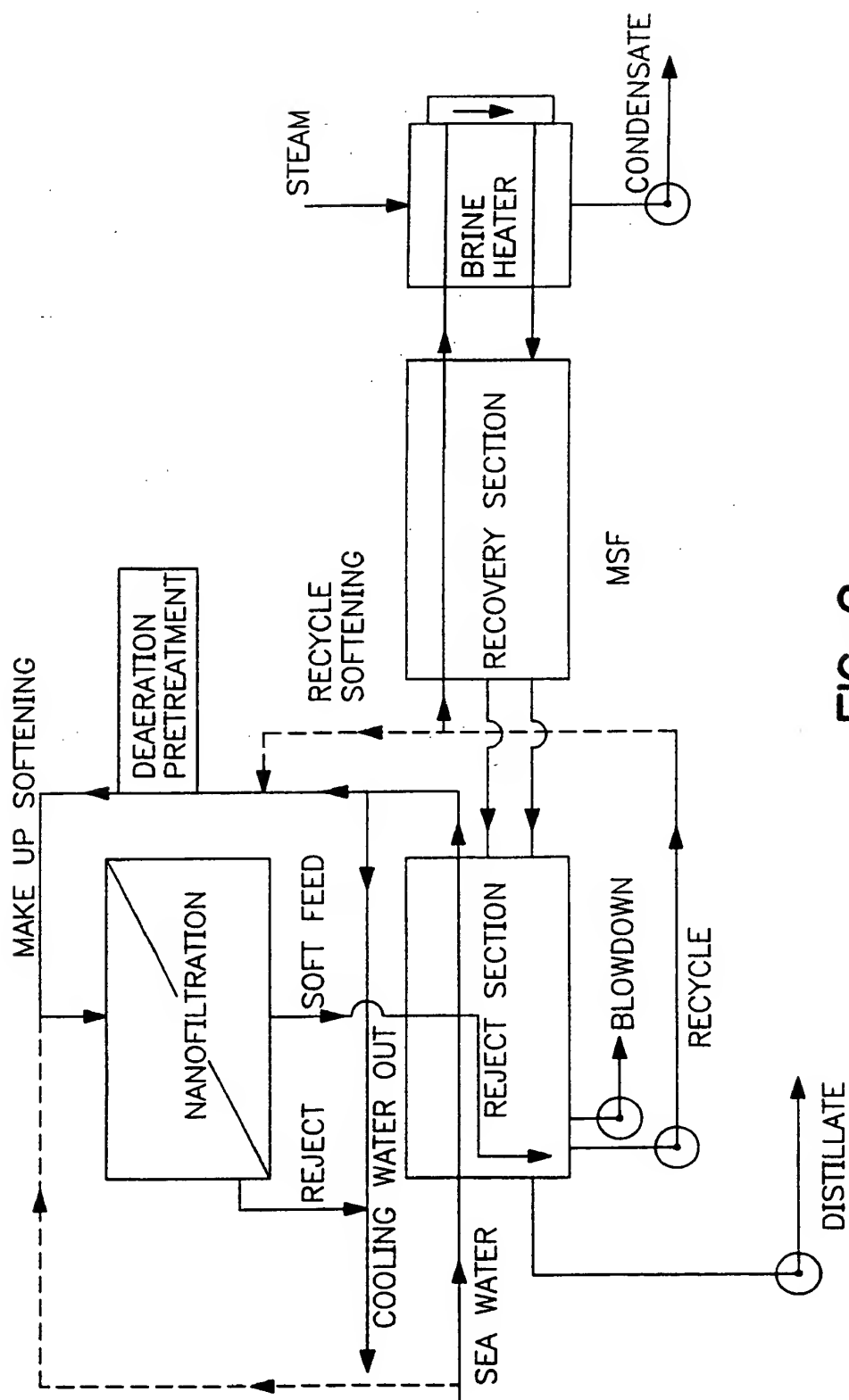


FIG. 1





**SUBSTITUTE SHEET (RULE 26)**

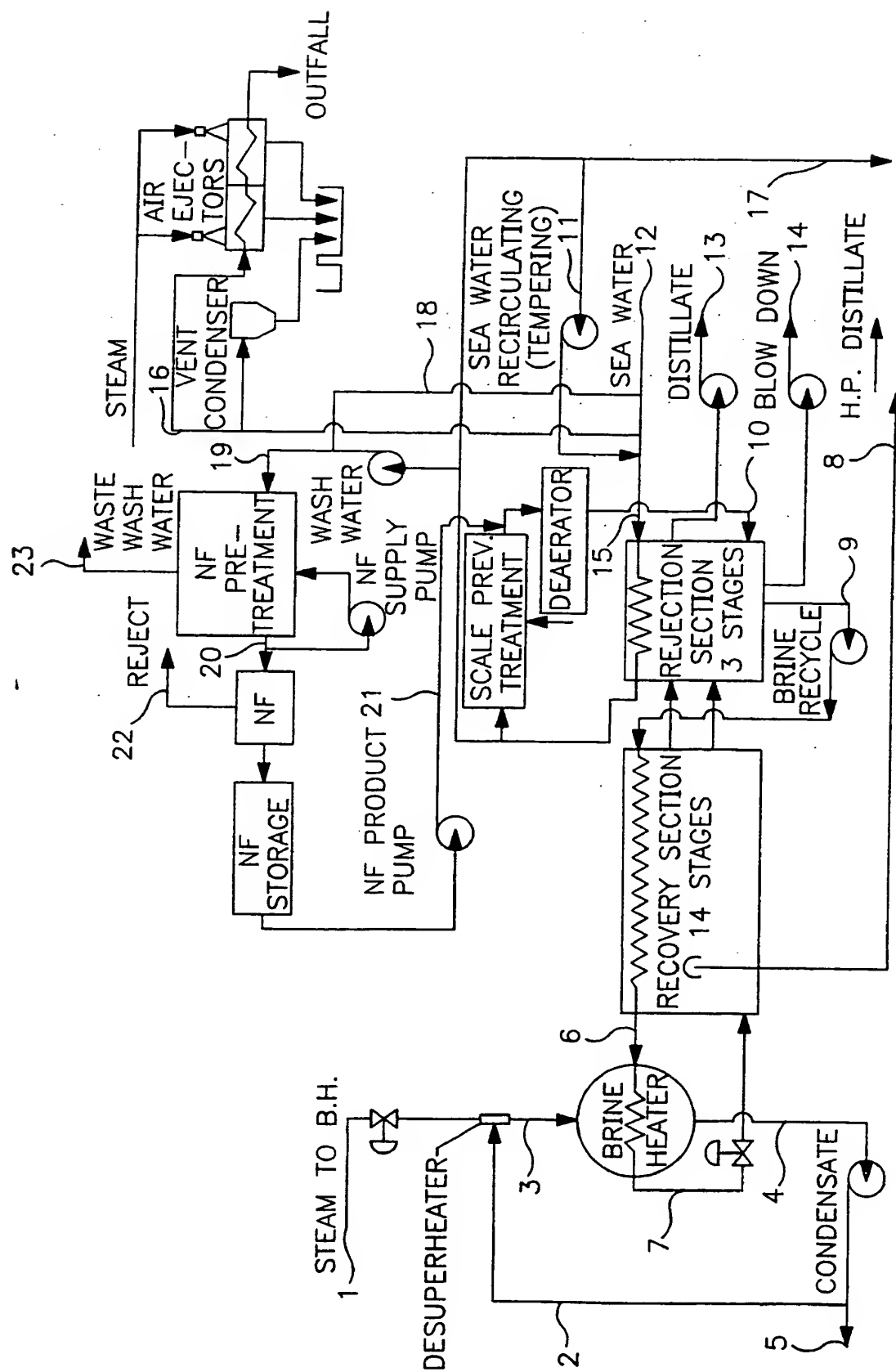


FIG. 3

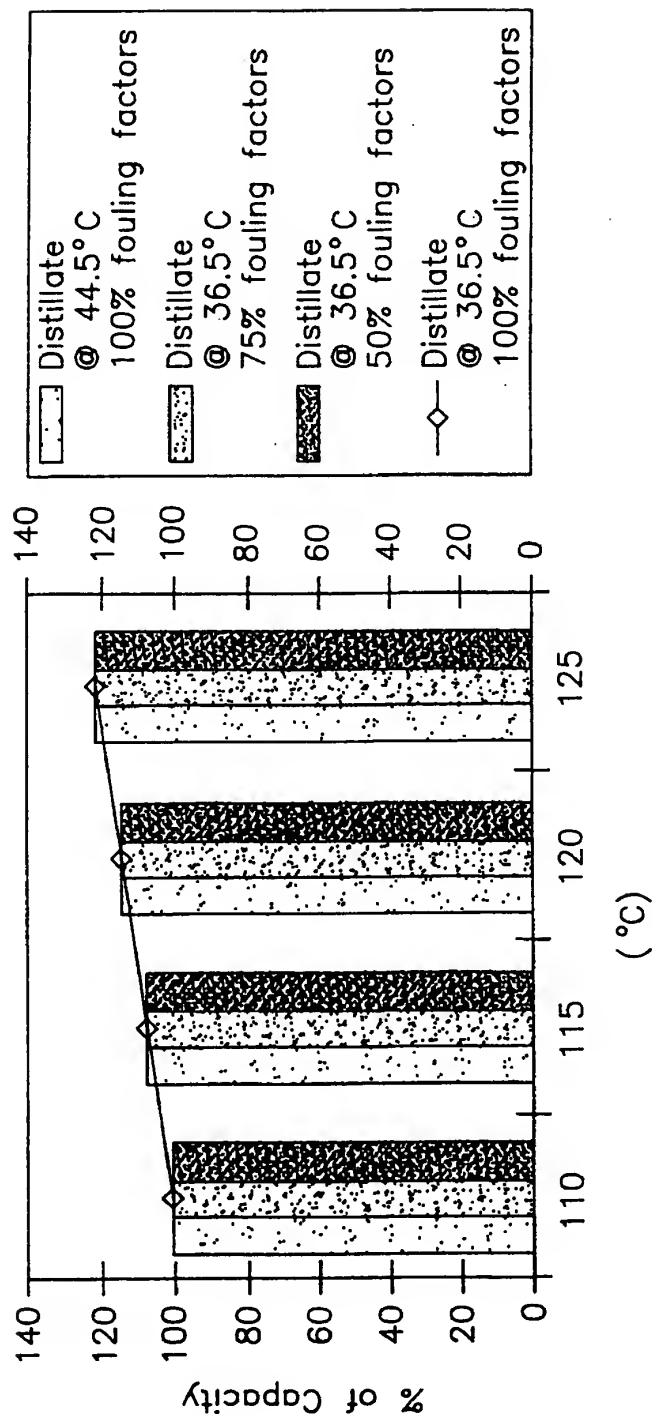


FIG. 4

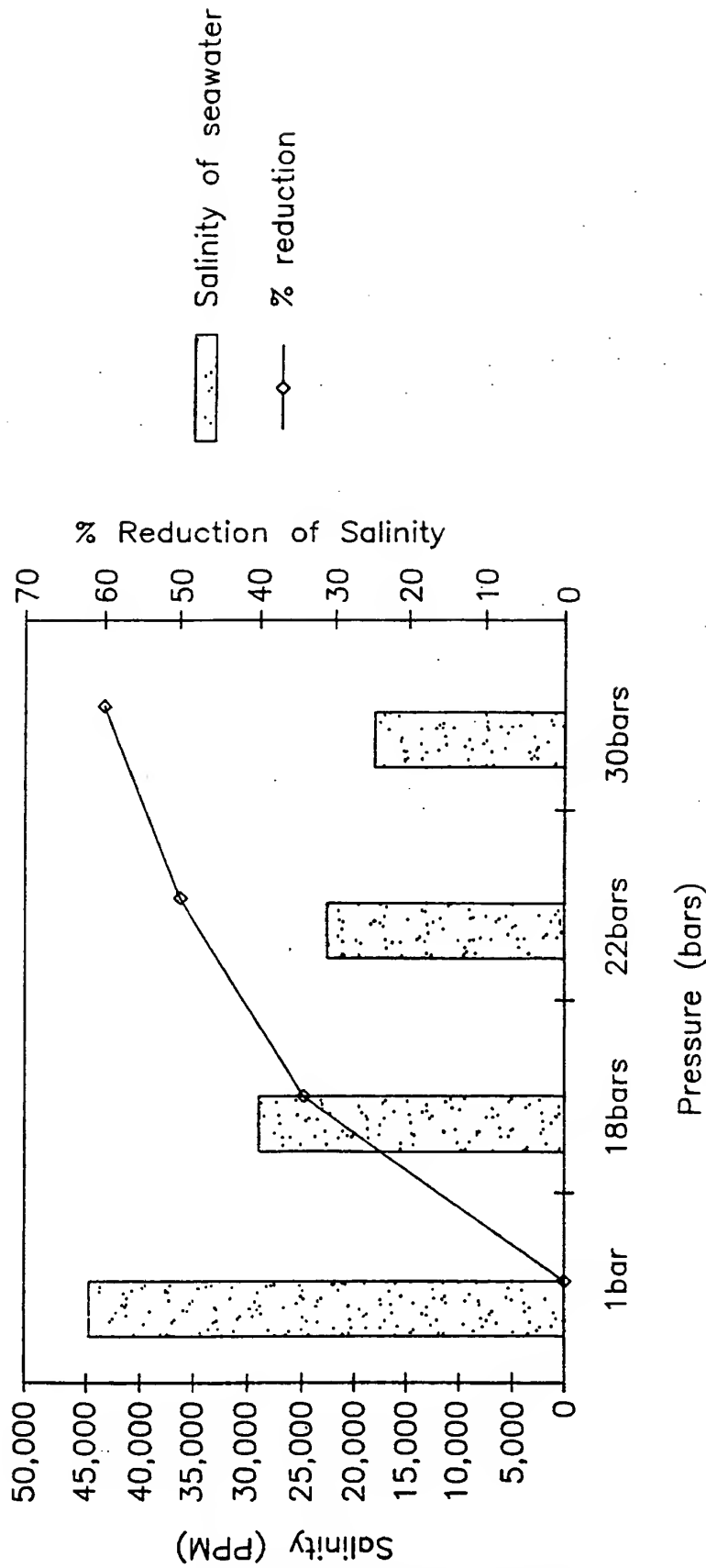


FIG. 5

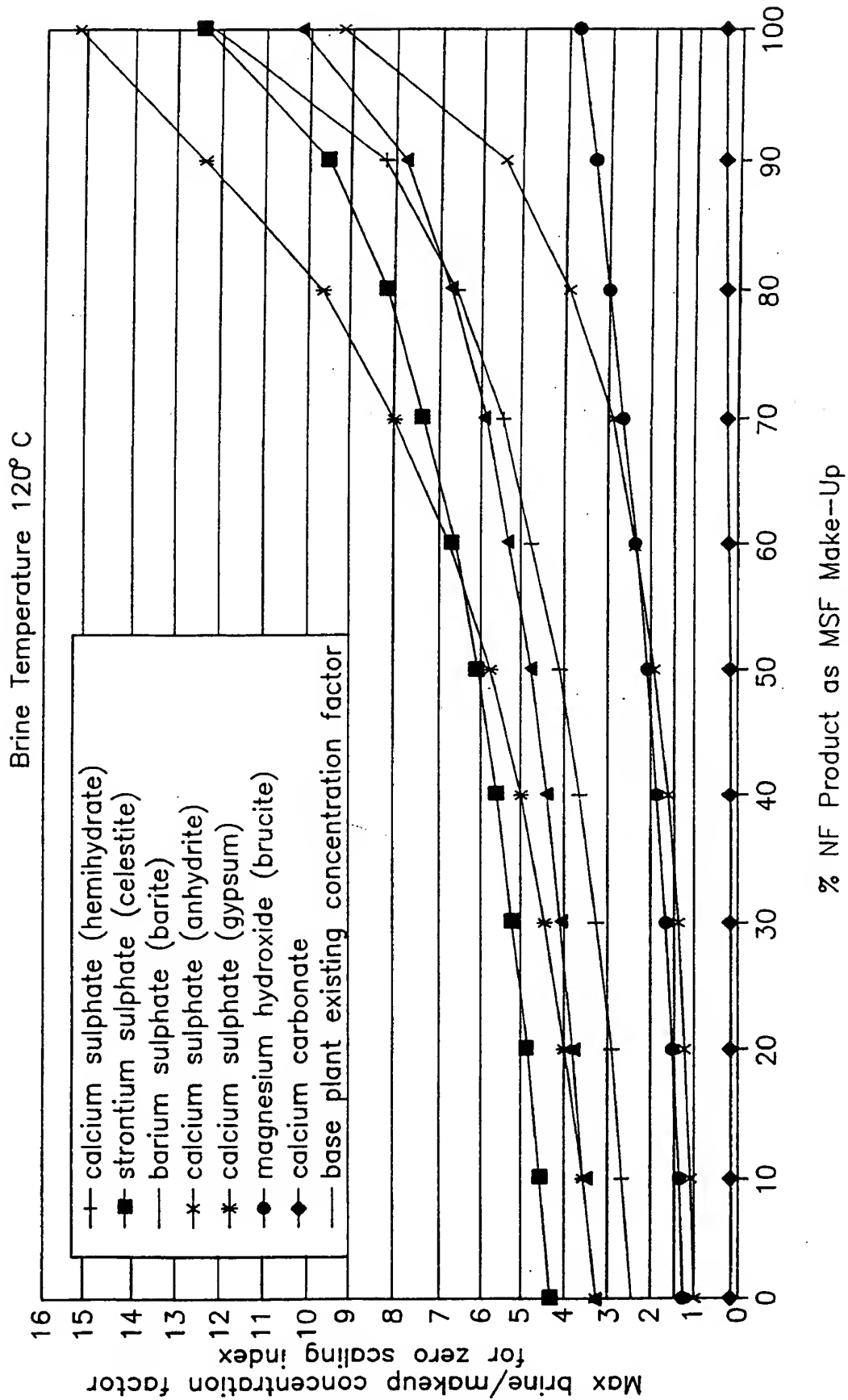


FIG. 6

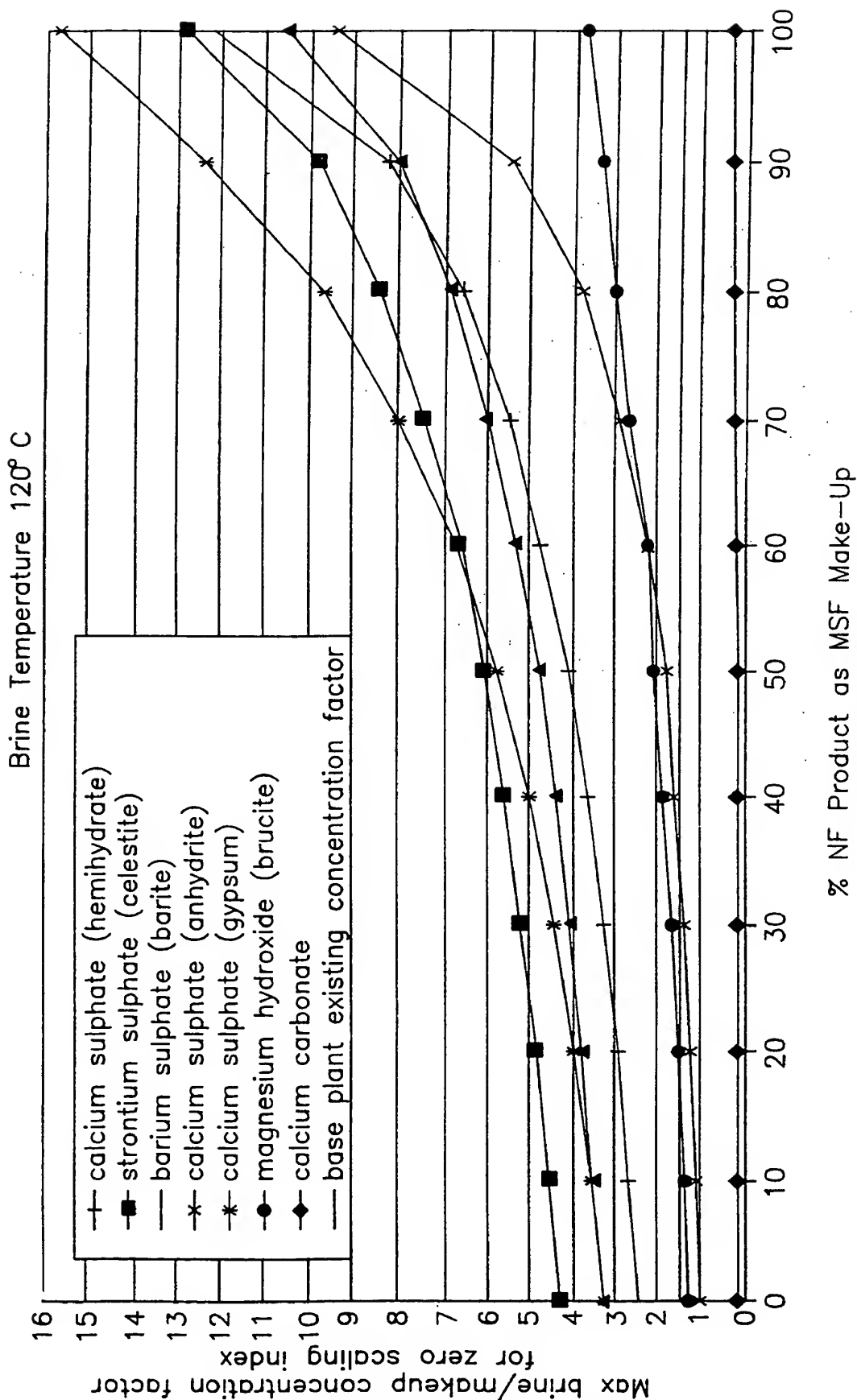


FIG. 7

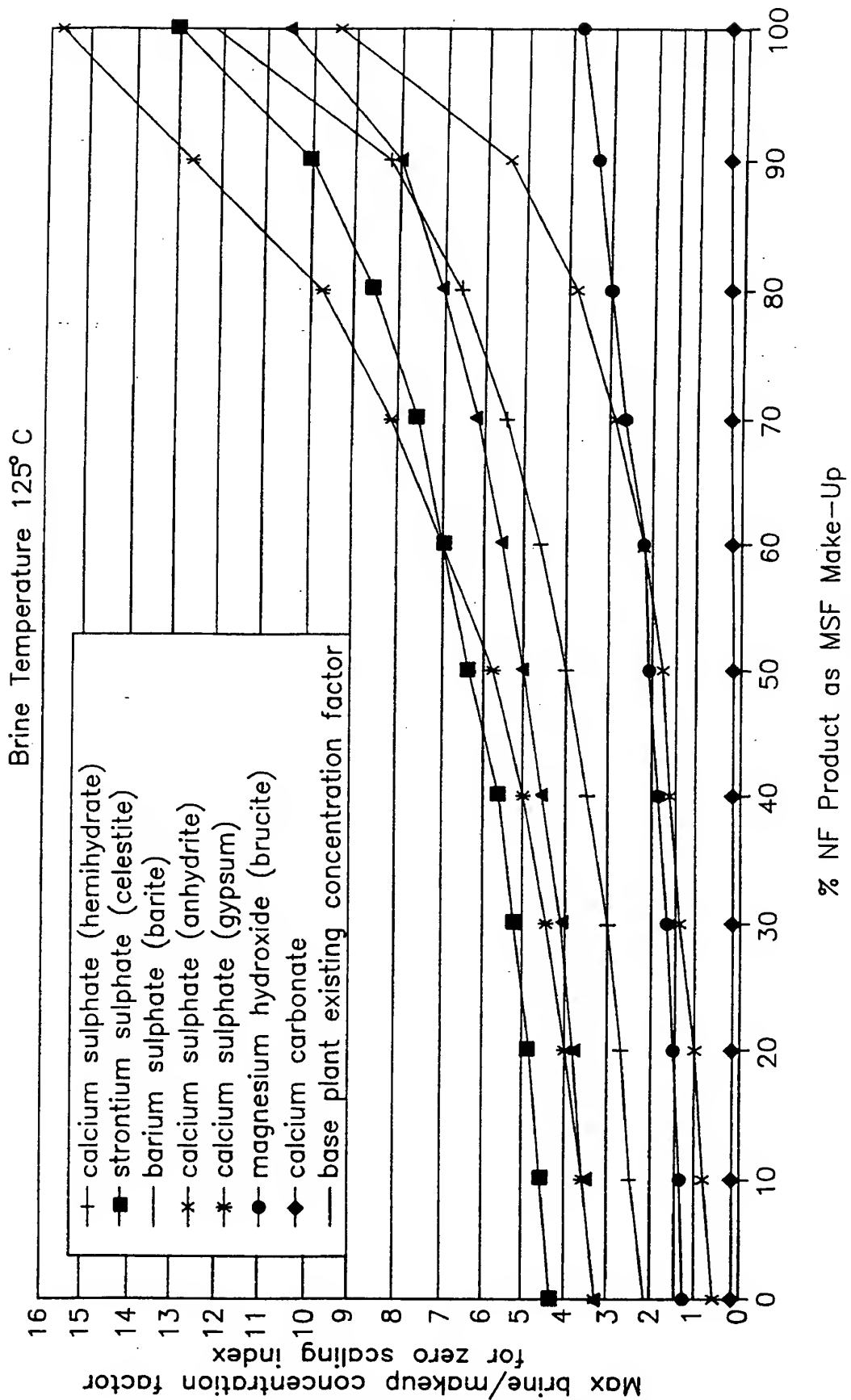


FIG. 8

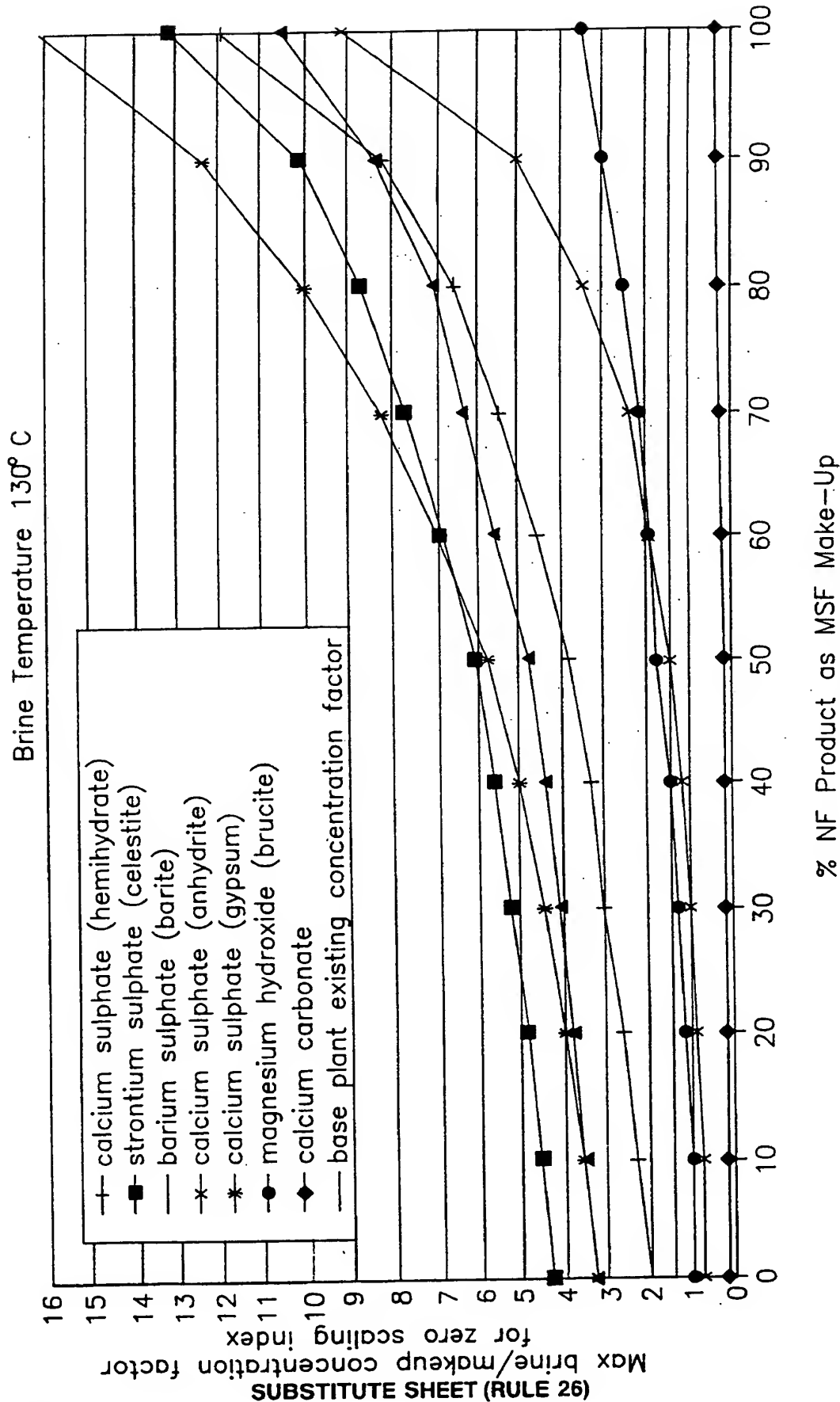


FIG. 9

SUBSTITUTE SHEET (RULE 26)



## INTERNATIONAL SEARCH REPORT

Intern. Patent Application No

PCT/US 00/22448

## A. CLASSIFICATION OF SUBJECT MATTER

IPC 7 C02F1/04 C02F1/44 B01D1/26 B01D3/06 B01D61/02

According to International Patent Classification (IPC) or to both national classification and IPC

## B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)

IPC 7 C02F B01D

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

EPO-Internal, WPI Data, PAJ, INSPEC, COMPENDEX

## C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	US 3 725 267 A (GELBLUM P) 3 April 1973 (1973-04-03) abstract; figure 2 column 3, line 53 - line 70 column 4, line 21 - line 34	24
A	---	1-4,6, 19,20
	-/--	

☒ Further documents are listed in the continuation of box C.☒ Patent family members are listed in annex.

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Date of the actual completion of the international search

27 November 2000

Date of mailing of the international search report

04/12/2000

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C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT		
Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
X	PATENT ABSTRACTS OF JAPAN vol. 006, no. 110 (C-109), 22 June 1982 (1982-06-22) -& JP 57 038982 A (BABCOCK HITACHI KK), 3 March 1982 (1982-03-03) abstract; figure 1 -& DATABASE WPI Derwent Publications Ltd., London, GB; AN 1982-29522E XP002153739 abstract	24
A	---	1
A	WO 99 16714 A (SALINE WATER CONVERSION CORP ; HASSAN ATA M (US)) 8 April 1999 (1999-04-08) cited in the application abstract; claims 1-4, 11, 19; figures 2, 9 page 20, line 9 - line 18 tables 6, 7	1, 3-10, 18-21, 24, 25
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## INTERNATIONAL SEARCH REPORT

Intern. Patent Application No

PCT/US 00/22448

## C.(Continuation) DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
A	<p>PATENT ABSTRACTS OF JAPAN vol. 008, no. 218 (C-245), 4 October 1984 (1984-10-04) -&amp; JP 59 102492 A (MITSUBISHI JUKOGYO KK), 13 June 1984 (1984-06-13) abstract; figure 1 -&amp; DATABASE WPI Derwent Publications Ltd., London, GB; AN 1984-184690 XP002153741 abstract</p> <p>-----</p>	24, 26

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Information on patent family members

International Application No

PCT/US 00/22448

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